Final Technical Report

Influence of Solutocapillary Convection on Macrovoid Defect Formation in Polymeric Membranes

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Principal Investigator: Alan R. Greenberg
Department of Mechanical Engineering
University of Colorado, Boulder, CO 80309-0427
Phone: (303) 492-6613; email: alan.greenberg@colorado.edu

Co-Principal Investigator: William B. Krantz
Department of Chemical and Materials Engineering
University of Cincinnati, Cincinnati, OH 45221-0018
Phone: (513) 556-4021; email: bkrantz@alpha.che.uc.edu

Co-Principal Investigator: Paul Todd
SHOT, Inc
7223 Winddance Parkway
Greenville, IN 47124
Phone: (812) 923-1859; email: ptodd@shot.com

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1. Overview

The focus of this research project involved the dry-cast process for polymeric membrane formation, whereby evaporation of solvent from an initially homogeneous polymer/solvent/nonsolvent solution results in phase separation and the formation of polymer-rich and polymer-lean phases. Under certain conditions the polymer-lean phase gives rise to very large and usually undesirable, tear-drop-shaped pores (size ~10-50 μm) termed macrovoids (MVs). Although in many cases the presence of MV pores has deleterious effects on membrane performance, there are a number of innovative applications where the presence of such pores is highly desirable.

Although researchers have proposed a variety of mechanisms for MV formation over the past three decades, two main hypotheses are currently favored: one asserts that MV growth can be attributed solely to diffusion (the diffusive growth hypothesis), whereas the other states that solutocapillary convection (the SC hypothesis) at the MV interface contributes to growth. According to the diffusive hypothesis, MVs initiate when stable (i.e., outside the binodal) polymer solution is present directly ahead of a newly formed layer of polymer-poor nuclei near the top of a freshly demixed film. After MV initiation, growth occurs by diffusion of primarily solvent to the MV nuclei, when the diffusional flow of solvent from the polymer solution into the nuclei is larger than the flow of nonsolvent from the nuclei into the polymer solution. Because this growth mechanism does not involve any force balance on the MV, buoyancy effects are presumed to have no effect on MV size. Since diffusion alone cannot account for MVs that are observed to form on the short time scale (as little as 1-5 s) typical for dry-casting, the SC hypothesis contends that MV growth is governed by a balance among the various forces including the solutal Marangoni convection force (solutocapillary convection), viscous drag force, and the buoyancy force.

Despite these prior studies, many aspects of membrane morphology development including the initiation and growth of macrovoid pores are not well understood. Consequently, the overall goal of this research was to obtain a more comprehensive understanding of the fundamental mechanism of MV growth. This research incorporates a coupled modeling and experimental approach to test a solutocapillary convection hypothesis for the growth of macrovoid pores in polymeric membranes. Specifically, we utilized a modification of the first principles model developed by two of the PIs (ARG and WBK) for dry-cast CA membranes. For the experimental component, two separate and mutually complementary approaches were used to study MV growth. In the first, membranes cast in a zero-g environment aboard the NASA KC-135 aircraft were compared with those cast on the ground to assess the effect of the buoyancy force on membrane morphology and MV size and shape. In the second approach, videomicroscopy flow visualization (VMFV) was utilized to observe MV formation and growth in real time and to assess the effect of surface tension on the MV growth dynamics. As a result of these fundamental studies, our research group advanced a new hypothesis for MV pore development in polymeric membranes. Details of this work have been reported in the publications and presentations cited in section 3.

2. Summary of Major Findings

In order to assess the effect of buoyancy force by comparing morphologies of membranes cast in a microgravity environment to those cast on the ground, a special membrane casting apparatus (MCA) was necessary. The MCA would ensure having identical conditions for membrane casting in the laboratory (ground-based experiments) as well as onboard the KC-135 aircraft. The first MCA was flown in an October 1998 KC-135 mission. The results qualitatively indicated that buoyancy inhibits MV growth. However, rigorous statistical analysis of the data could not be performed because of certain limitations in the MCA design, which became apparent only after testing its operation in flight. These limitations included uneven machining of the substrate that led to membranes of a non-uniform thickness, and excessive drag associated with the firing mechanism designed to obtain instantaneous casting, which led to "sloshing" of the casting solution. The qualitative insights gained from this study were published in a manuscript in the *Journal of Membrane Science* (2002).

Based upon these insights, the MCA design was revised, and a modified MCA was fabricated. These design details were described in an article published in the American Chemical Society Symposium Series book "Polymer Processing in Low Gravity", edited by J. Pojman (2001). The modified MCA had larger casting wells, polished surfaces to enable casting of samples of uniform thickness, and a different sliding arrangement to minimize sloshing. Real-time monitoring of the demixing and membrane formation process was incorporated using laser probes in two of the wells. The MCA was utilized for microgravity membrane casting in a KC-135 flight in February 2000. These experiments utilized a three-factor experimental design with three levels of casting solution composition, two levels of surfactant addition, and three levels of gravitational conditions; the initial thickness of the casting solution was kept constant at 150 microns and served as a control variable. Analysis of the membrane morphology including the size and distribution of the MVs indicated that the casting solution composition as well as the presence of surfactant had a statistically significant effect on the MV morphology for membranes formed with the modified MCA assembly. The results of this study are described in a paper that was published in *Desalination* (2002), as well as presented at the International Conference on Membranes and Membrane Processes (ICOM) that was held in Toulouse, France in July 2002.

Although the modified MCA led to a significant improvement in our ability to cast the membranes in microgravity, the definitive evidence linking solutocapillary convection to MV growth could not be obtained due to several unanticipated problems, which have been described in a number of the references in section 3. Overall, our substantial experience in MCA operation was extremely valuable in designing a new MCA for the more challenging wet-casting process that is currently being studied through another NASA project (NAG3-2541) at the University of Cincinnati (PI: WBK). This new MCA is based on a radically different design concept, and incorporates many innovative features. This new MCA was flight tested in May 2002, and membranes were prepared using the wet-casting process. The unit performed well with only minor difficulties. One notable observation was that membranes cast with the MCA tethered to the aircraft were much more non-uniform compared to those cast in an untethered MCA. Clearly, the aircraft engine vibrations transmitted through the tethering cable affected the membrane structure. This was a significant finding since all previous ground-based casting was achieved by placing the MCA on a general work platform. Apparently, normal room vibrations can introduce a degree of randomness and uncertainty in the membrane morphology, and therefore are undesirable in a strict experimental study. Hence, maintaining consistency between the casting aboard the aircraft and on the ground requires a vibration-free environment in the laboratory.

We also employed experiments to quantify the surface tension effects directly through flow visualization techniques using casting solutions containing different surfactant concentrations. These videomicroscopy flow visualization (VMFV) experiments yielded unique insights into the

MV growth dynamics, and resulted in the development of a modified hypothesis for MV growth. The VMFV experiments produced two significant observations: (1) the presence of solutocapillary driven convection cells near the MV surface, which significantly enhances mass transfer to the growing MV, and (2) three distinct phases of MV development - fast initial growth, slow growth, and collapse. Extremely rapid initial growth is thought to occur owing to coalescence of dispersed phase microdroplets with the emerging MVs. The modified hypothesis postulates that a homogeneous supersaturated solution layer must exist between the demixed fluid layer and the homogeneous stable solution layer to insure net mass transfer to a growing MV. Fast growth also involves mass transfer to the MV whose surface is entirely immersed in the homogeneous supersaturated solution layer. Slow growth involves net mass transfer to the MV across its surface in contact with the homogeneous supersaturated solution layer and mass transfer from its surface that extends into the homogeneous stable solution layer. Active collapse is thought to occur owing to skin formation at the MV surface whereas passive collapse occurs when the mass transfer from the MV surface in the homogeneous stable solution layer exceeds that to it in the homogeneous supersaturated solution layer. A manuscript describing these key qualitative insights has been published in the *Journal of Membrane Science* (2003). In addition, quantitative results including the effect of surfactant concentration on MV occurrence as well as on the interfacial velocities were published in *Desalination* (2002).

The dry-casting model developed by the project PIs (ARG and WBK) was modified to account for purely diffusive evaporative solvent transfer in the gas phase in low-g rather than free convection gas-phase mass transfer that applies in 1-g. This model was used to predict the time for the completion of phase separation. The excellent agreement obtained between these modeling and experimental results is impressive in view of the fact that this model solves the coupled multi-component diffusion and energy equations using Flory-Huggins theory to describe the highly non-ideal solution thermodynamics and does not employ any curve-fitting parameters, i.e., this is a first-principles, fully predictive model. The measured and predicted values for the phase-separation times agree better than the PIs found for laboratory-based 1-g studies; this is because the low-g eliminates the buoyancy-induced convection in the gas phase that is more difficult to model accurately than the purely diffusive gas-phase mass transfer that occurs in the low-g experiments. This is another advantage of carrying out studies to understand the influence of solutocapillary convection on structure development in polymeric membranes in a low-g environment. The comparison between model predictions and experimental results was described in a *Journal of Membrane Science* manuscript (2002).

Overall, the key insights obtained from this project include:

- MV occurrence is facilitated by a lower solvent-nonsolvent ratio. This suggests that the rate of demixing affects MV formation and growth.
- The MV growth dynamics appear to be rather complex. MV growth occurs in distinct phases that include rapid initiation, slow growth, and incorporation into the de-mixed membrane structure. There is a two-way transfer of material between the MV and the surrounding unmixed casting solution. Our work has established that MVs can "disappear" through passive (the MV material diffuses to the surrounding solution) or active collapse (the MV material is pumped into a neighboring growing MV.
- MVs initially grow explosively out of the de-mixing front. This extremely rapid initial growth phase suggests the presence of a supersaturated phase immediately preceding the MV nuclei formation.

- The role of surfactants and hence surface tension is manifested via effects on the free energy available for the coalescence of polymer-poor nuclei to form MVs.

Although these results do not comprehensively link solutal-Marangoni convection to MV growth, the studies yielded some very important and critical insights into the MV formation and growth dynamics. In addition, recent work has confirmed that our evaporative casting experiments complement the wet-casting studies being conducted at the University of Cincinnati. In cooperation with the University of Cincinnati team (PI: WBK), we are planning additional dry-casting tests using a new MCA unit in an upcoming KC-135 flight in May 2003. Moreover, we are finishing extensive ground-based membrane casting using a vibration table and a light reflectometry apparatus to enable comparison between model predictions and experimentally observed de-mixing times. We plan to publish the results obtained from this latest work.

3. Accomplishments

This research project has meaningfully involved graduate and undergraduate students, contributed to the generation of intellectual property, and has resulted in a number of publications and presentations. These achievements are summarized in the following sections.

Students

One Ph.D. student supported by this project received his Ph.D. degree in 1998 and is currently employed by Bend Research, a small membrane company. An M.S. student supported by this project received his degree in 1999 and is employed by the Intel Corporation in their manufacturing operations. Another Ph.D. student involved with aspects of the modeling studies of this project is employed by the IBM Corporation in their materials characterization operations. A current Ph.D. student who has received limited support from this project to address some final computational issues with the current model is scheduled for her Ph.D. defense in May 2003, and has an opportunity for employment with a start-up membrane company.

The project was able to provide a unique opportunity for undergraduate research experiences. In particular, the contributions of Jeremy Zartman to this study have been recognized by his co-authorship of project manuscripts and presentations and were pivotal in his recent award of a prestigious Goldwater Scholarship. In addition, Mr. Zartman participated in our June 2002 KC-135 flight.

Patent Activity

As a direct result of participating in the project research studies, an undergraduate student formulated a device and method using a non-uniform electric field to control the pore structure of porous membranes and films. Initial studies indicated that this device could be used to reduce or eliminate macrovoid defects. The results of this research were sufficiently compelling that the undergraduate student was chosen as a BF Goodrich Collegiate Inventor of the Year (2000). This prestigious award carried a cash prize as well as induction of the student in the National Inventors Hall of Fame in Akron, Ohio. The student was subsequently employed during the summer by a major membrane manufacturer and worked on the further development of the patent technology under an agreement with the University of Colorado. A patent for this technology was issued in 2002 (Apparatus and Method for Controlling Pore Size in Polymeric Membranes and Thin Film, issued on November 12, 2002, U.S. Patent Number 6,479,007 B1, A. Greenberg, W.B. Krantz, A. Niece, and P. Todd.). New insights regarding uses of this technology provided the basis for a July 2002 proposal submission to NASA, Use of Low-G to

Study Electromagnetic Field Templating of Pore Structure in Polymeric Membranes, by two of the PIs (ARG and WBK) in response to NRA-01-OBPR-08.

Publications and Presentations

Book

Todd, P., Pekny M.R., Zartman, J., Krantz, W.B. and Greenberg, A.R. "Instrumentation for Studying Polymer Film Formation in Low Gravity." in Polymer Research in Microgravity: Polymerization and Processing. J. P. Downey and J.A. Pojman, eds., ACS Symposium Series 793, 126-137, 2001.

Journal

Matthew P.R., Zartman, J., Greenberg A.R., Todd, P., and Krantz, W.B. Flow visualization during macrovoid pore formation in dry-cast cellulose acetate membranes. *Journal of Membrane Science*, 211, 71-90 (2003).

Pekny, M.R., Greenberg, A.R., Khare, V., Zartman, J., Krantz, W.B., and Todd, P. Macrovoid pore formation in dry-cast cellulose acetate membranes: buoyancy studies. *Journal of Membrane Science*, 205, 11-21 (2002).

Khare, V.P., Greenberg, A.R., Zartman, J., Krantz, W.B., and Todd, P. Macrovoid growth during polymer membrane casting. *Desalination*, 145, 17-23 (2002).

Proceedings

A.R. Greenberg, V.P. Khare, J. Zartman, W. B. Krantz, and P. Todd, "Macrovoid Defect Growth During Evaporative Casting of Polymeric Membranes," NASA Microgravity Materials Science Conference, Huntsville, AL, June 2002.

P. Todd, J.C. Vellinger, S. Sengupta, M.G. Sportiello, A. R. Greenberg, and W.B. Krantz, "Sliding-Cavity Fluid Contactors in Low-Gravity Fluids, Materials and Biotechnology Research," Proceedings of the Microgravity Transport Processes in Fluid, Thermal, Biological and Materials Sciences II, Banff, Alberta, Canada, October 2001.

V. Khare, A. R. Greenberg, W.B. Krantz, H. Lee, P. Todd and S. Dunn, "Polymer Thin Film Formation on Low-Gravity Aircraft and on ISS," AIAA Paper 2001-5024, Conference & Exhibit on International Space Station Utilization—2001, Cape Canaveral, FL, October 2001.

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Pekny M.R., Zartman, J. Greenberg A.R., Todd P. and Krantz W.B. "Influence of Solutocapillary Convection on Macrovoid Defect Formation in Polymeric Membranes." NASA Microgravity Materials Science Conference 2000, N. Ramachandran, N. Bennett, D. McCauley, K. Murphy and S. Poindexter, eds., NASA/CP-2001-210827, 273-277 (2001).

Presentations

Khare, V.P., Greenberg, A.R., "Macrovoid formation during dry casting for the cellulose acetate/acetone/water system," Annual Conference of the North American Membrane Society, Jackson Hole, WY, May 2003, accepted for presentation.

Khare, V.P., Greenberg, A.R., Zartman, J., Krantz, W.B., and Todd, P. "Macrovoid growth during polymer membrane casting." Presented at the International Conference on Membranes, Toulouse, France, July 2002.

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Zartman, Z., Todd, P., Greenberg, A.R., and Krantz, W.B. "Microscopic flow visualization in demixing fluids during polymeric membrane formation," SWARM-AAAS 76th Annual Meeting, Las Cruces, April 9-12, 2000.

Pekny, M.R., Zartman, Z., Greenberg, A.R., Krantz, W.B., and Todd, P. "Influence of buoyancy and surfactant solutes on macrovoid defect formation in dry-cast cellulose acetate membranes," 219th National Meeting of the American Chemical Society, San Francisco, March 30, 2000.